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ECONOMICS**
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Wet oxidation of process wastewaters with high organic
content

Ph.D. Thesis

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2016

Introduction

The world's freshwater resources are finite, the amount per capita is decreasing drastically. The protection of water quality, i.e. the purification of wastewater is a key issue and is an important research field. Returning the wastewaters into the natural circulation is essential also. Beside the domestic consumption, the energetic, food, and chemical industries as well as the agriculture are the highest consumers. Huge amount of utilized water gets back into the nature with small contamination, untreated. These are primarily cooling and irrigation waters (for example 95-98% of the water used by energy production, 30-40% of the consumption for agricultural application). The amount of water used within industrial processes is smaller, but significant (as solvent, reactant, etc). In these processes the water becomes more contaminated, so its treatment is needed before returning to the nature¹.

The disposal of process wastewaters (PWWs) of industrial, or agricultural origin is a complicated task. The composition of these mixtures is unknown or only partially known. The detailed chemical analysis of these wastes would be too costly. The typical examples for such PWWs are of pharmaceutical origin². These water-containing liquid wastes with high organic content can't be treated as the municipal wastewater, because they contain often bioactive compounds and are classified as hazardous wastes.

Wet air oxidation (WAO) is a known method to treat highly concentrated liquid organic wastes. The first patent application was dedicated to Zimmermann and Diddams in 1960³, which describes treating of pulp and papermill wastes. The WAO is a technology with high energy consumption. It applies high temperature, high pressure and long reaction time to mineralize the contaminants. To

¹ Shannon MA, Bohn PW, Elimelech M, Georgiadis JG, Mariñas BJ, Mayes AM. *Nature*. 452 (2008) 301–310.

² Gadipelly C, Pérez-González A, Yadav GD, Ortiz I, Ibáñez R, Rathod VK, et al. *Ind Eng Chem Res*. 53(29) (2014) 11571–92.

³ Zimmermann FJ, Diddams DG. *TAPPI*; 43 (1960) 710-715.

increase the reaction rate is an important research task. The outcome could be the decrease of the temperature and the pressure. The use of homogeneous catalysts in WO can be a solution but its disadvantage is the need of recovery of the catalyst. This is a strict requirement not just because of the recycling, but because of the toxic effect of the remaining metal ions in the reaction mixture. Several research groups deal with development of heterogeneous catalysts for WAO (catalytic wet air oxidation, CWAO).

The development of active and stable catalyst for treating of liquid pharmaceutical wastes is a challenging task, because they contain different substances with concentration of wide range. The main problem is that the active phase of the catalyst could be leached into the reaction mixture among CWAO conditions (high pressure and high temperature) even at basic pH. The chemical properties of the precious metals promise better stability but increase the costs of the process. However the higher activity and the longer lifetime could compensate this drawback. The presence of a heteroatom, like nitrogen, in the molecule to be oxidized will increase the chance of leaching in case of precious metal catalysts also. Ru, Pt were active catalysts in oxidation of organic acids⁴, but had extremely high leaching rate in the oxidation of *N*-containing compounds (like *N,N*-dimethylformamide (DMF), methylamine, etc.)^{5,6,7}.

There are some references, which describe that the oxides of precious metals are less stable than the metallic form⁸. Earlier in our institute a ruthenium-iridium (Ru-Ir) containing titanium (Ti) mesh

⁴ Yang S, Besson M, Descorme C. Catalytic wet air oxidation of succinic acid over Ru and Pt catalysts supported on CexZr1 - xO2 mixed oxides. *Appl Catal B Environ.* 165 (2015) 165 1-9.

⁵ Grosjean N, Descorme C, Besson M. *Appl Catal B Environ.* 97(1–2) (2010) 276–283.

⁶ Lousteau C, Besson M, Descorme C. *Catal Today.* 241 (2015) 80–85.

⁷ Sun G, Xu A, He Y, Yang M, Du H, Sun C. *Appl Catal B Environ.* 156(1–3) (2008) 335–341.

⁸ Yu C, Zhao P, Chen G, Hu B. *Appl Surf Sci.* 257(17) (2011) 7727–31.

was tested in the wet oxidation (WO) of real pharmaceutical wastes⁹. This mesh was a stable and active catalyst despite that its precious metal content was at least partially in oxides. The catalytic activity and stability of this mesh were better than that of the powder form catalysts¹⁰.

Several compounds with nitro, amino, amide functional groups or with heterocyclic ring are usually present in the pharmaceutical liquid wastes. As the conversion of the nitrogen content to N₂, or to NH₃ is an essential step in the oxidation reaction, therefore DMF and paracetamol (PAR) were chosen as model substrates. The CWAO of the latter is missing in the literature¹¹ (however it is frequently detectable in the effluent of wastewater treatment plants (WWTPs) and in natural waters¹²).

The oxidation properties of wastewaters of complicated composition are permanently changing. In order to increase their biodegradability additional treatments may become necessary, if the partial WAO or CWAO are not sufficient. In such cases combination of different techniques is required. The preliminary experiments are necessary for characterizing all kinds of wastewaters and as result one can decide about their treatment methods, about the optimal sequence of disposal processes.

The design of experiments (DOE) is well known for long time and can be applied for optimization of research and operating parameters^{13,14}. The DOE was used for the WO during my research

⁹ Hosseini AM, Bakos V, Jobbágy A, Tardy G, Mizsey P, Makó M, et al. *Period Polytech Chem Eng.* 55(1) (2007) 3–10.

¹⁰ Hosseini AM, Tungler A, Schay Z, Szabó S, Kristóf J, Széles É, et al. *Appl Catal B Environ.* 127 (2012) 99–104.

¹¹ Quesada-Peñate I, Julcour-Lebigue C, Jáuregui-Haza UJ, Wilhelm AM, Delmas H. *J Hazard Mater.* 221–222 (2012) 131–8.

¹² Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, et al. *Environ Sci Technol.* 36(6) (2002) 1202–11

¹³ Lundstedt T, Seifert E, Abramo L, Thelin B, Nyström Å, Pettersen J, et al. *Chemom Intell Lab Syst.* 42(1–2) (1998) 3–40.

¹⁴ Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escalreira LA. *Talanta.* 76(5) (2008) 965–77.

work as a tool that made possible more precise comparison of different catalysts with the accurate description of parameter-dependence of reaction rates.

Our research group participates in the development of a technology which combines two methods. Two kinds of oxidations are carried out in one device without additional oxidative agent beside oxygen. The oxidative conversion of phenol could be detected even on room temperature, under oxygen pressure in a stainless steel autoclave. It was equipped with a Ti window, through which the high energy electron beam was introduced¹⁵. The method has to be developed further for practical application.

Objectives

The presented research work is the subtask of a complex project (Swiss-Hungarian Cooperation, SH/7/2/14), this means that I could rely on the former results and conclusions of the project. One of the most important observations was that the PWWs of the pharmaceutical industry became biodegradable after mixing them with municipal wastewater. The majority of municipal wastewaters are deficient in carbon, so the denitrification process can't be completed. The additional carbon source (methanol) can be replaced in the WWTP by feeding PWWs of the pharmaceutical industry which wastes are not toxic, or can be made biodegradable with pretreatment¹⁶.

WAO is a suitable technology for the partial oxidation of such wastewaters, the increase of its efficiency is a substantial task because of the necessary high temperature and pressure. The investment and operational costs are high, have to be decreased.

A possible method for increasing the efficiency was the combination of WO with high energy electron beam irradiation. This type of irradiation has a radical generating effect especially in the

¹⁵ Chamam M, Földváry CM, Hosseini AM, Tungler A, Takács E, Wojnárovits L. *Radiat Phys Chem.* 81(9) (2012) 484–8.

¹⁶ Tardy GM, Bakos V, Jobbágy A. *Water Sci Technol.* 65(9) (2012) 1676–83.

presence of oxygen. A laboratory device has been built, delivering reproducible results using the combination of aforementioned methods, even at elevated temperature and pressure. The combination of the two methods was tested with a model wastewater, solution of sodium phenolate.

The further task of the research was the testing and investigation of expectedly active and stable catalysts among WO conditions, which can easily applied and scaled-up for practical purposes. Commercially available Ti meshes with precious metal content were chosen, which are used as electrode materials for electrolytic processes. The Ru-Ir/Ti catalyst was active in the WO of real and model (phenol and DMF containing) wastewaters. For the explanation of this activity, one had to explore the relationship between the activity and the oxidation state of the precious metals. Platinum (Pt), Ir and Ru containing meshes are available from the same company also, they were compared in WO and CWO of PAR.

Experimental methods

The research work affording the results of the dissertation can be divided into two parts: (1) material-testing methods characterizing the catalysts, determining their physical, chemical properties, (2) determination of their activity and stability in CWO reactions.

The material-testing methods were: prompt gamma activation analysis (PGAA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), and temperature programmed reduction (TPR). The measurements were carried out with the catalysts as received and after use also, in order to find relationship between structure and activity, stability.

The WO and CWO reactions were carried out at elevated temperature and under oxygen pressure in stainless steel autoclaves. The conversion was followed by chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN) measurements. The

precious metal containing Ti meshes were cut into pieces of appropriate size with respect to the autoclave dimensions. The pieces of the mesh were curved into a cylindrical mantle fitting to the autoclave. The catalytic activity measurements in the oxidation of DMF were implemented according to DOE with the commercial Ru-Ir/Ti mesh and with its reduced version. In the oxidation of PAR five different Ti monolith catalysts were tested and compared, with Pt, Pt-Ir, Ir, Ru and Ru-Ir content.

The device built for the combination of WO with high energy electron beam irradiation (EB) is on Fig. 1. The sealing and insulating materials used here were all radiation resistant. The rate increasing effect of radicals generated by the electron beam was investigated in the WO of sodium phenolate solution, the rates were compared with that of the non-catalytic (thermal) and catalytic reactions.

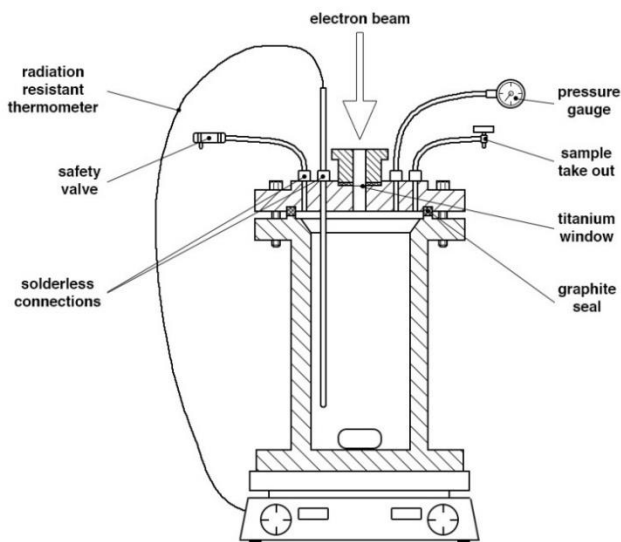


Figure 1. Special autoclave with irradiation possibility

Results

Combined EB-WO method

The comparison of the rate of thermal, catalytic and EB assisted reactions required the special device developed for this particular purpose. In the non-catalytic WO of phenolate at 150 °C and 25 bar during 2 hours the COD and TOC conversions were less than 20%. With the monolith Ru-Ir/Ti catalyst among the same conditions the COD conversion was 60%, in the EB-WO combined method the COD and TOC conversions were higher than 80% but during less than 30 minutes, the adsorbed dose was ~18 kGy. This means that the catalyst tripled, the EB increased to 15-fold the reaction rate.

CWO of DMF in experiments according to DOE, with catalyst of different oxidation state

The Ru-Ir/Ti was tested in received and in reduced state also, exploring the effect of the chemical valence state on the activity and stability. The reactions were carried out according to DOE, the evaluation of the results pointed out that there is no significant difference between the activities of the two catalysts of different pretreatments. The results of the material testing methods gave the explanation: regardless of the starting state of the surface Ru-Ir layer, nearly same composition upper layer was formed on both catalysts after 55 hours usage. The XPS measurements detected both M^0 and M^{IV} valence state precious metals on the surface. This means that the metallic species was oxidized among the reaction conditions, not losing its activity, but in the same time the oxide catalyst was partially reduced among the same conditions. According to the PGAA the Ru-Ir metal leaching remained within the measurement error, the stability of the catalyst was promising.

CWO of PAR

The commercially available Pt, Pt-Ir, Ir, Ru, Ru-Ir mono and bimetallic meshes, that is to say five different catalysts were tested in PAR oxidation. The catalysts were characterized with the

usual testing methods before and after the catalytic reactions. Two catalysts (Pt, Ru) being the most active, were tested after 100 hours usage also. The monometallic Ru is in oxide state on the Ti surface. Its Ru content is much less than the Pt content of the other catalyst, nevertheless the specific activity of the Ru containing one is higher. The Pt catalyst lost 23% of its precious metal content. The Ru content didn't change after 25+75 hours use (PGAA measurement), the Ru concentration (showing the presumable leaching) in the reaction mixture was 0.02 µg/L according to inductively coupled plasma mass spectrometry.

The biological oxygen demand (BOD) test of the final reaction mixture of the 75 hours experiment proved that the intermediates of the CWO of PAR are well biodegradable. The partial CWO of this substrate increases the biodegradability of wastewaters containing PAR.

The monolith catalysts, primarily the Ru containing meshes were characterized, that proved their advantages. They have moderate activity but good stability over against the powder form, high dispersion and high activity catalysts, which are prone to leaching. The practical application of the monoliths is preferred, as their handling is easier, the construction and design of the reactors is simple, the meshes need no pretreatment, commercial production of them is going on. It is worthwhile to develop further the preparation technique in order to increase their lifetime.

Theses

1. The rate of WO could be increased significantly with high energy electron beam irradiation. In the oxidation of sodium-phenolate solution on 150 °C and at 25 bar with Ru-Ir/Ti catalyst the reaction rate was tripled, with electron beam irradiation among the same conditions it was fifteen times higher. The combination of WO with high energy irradiation is an effective new advanced oxidation process (AOP), for its implementation a special new device has been developed. [3]

2. The Ru-Ir/Ti catalyst was active in the CWO of DMF also, it doubled the initial reaction rate. The precious metal content of the monolith catalyst did not decrease during approximately 55 hours usage, contrary to that of the high dispersion supported powder catalysts. [2]

3. In the WO of DMF the calculated result-surfaces by DOE and their sections at chosen parameters made the comparison of catalyst activities more reliable than it could be on the basis of randomly chosen measuring points. The resulting non-reduced rate equations, within the range of the measurement parameters, served as initial models for the design of scale-up experiments. [2]

4. It has been proven with surface investigation methods that on the Ru-Ir/Ti monolith catalyst after usage in the CWO of DMF the precious metals are present both in metallic and in oxide state as well regardless that the starting form was an oxide or a metallic form. This observation is consistent with the comparison of the catalysts activity with DOE which showed no significant difference. [2]

5. The CWO of PAR with Pt-, Ru-containing Ti-monolith catalysts could be carried out among milder conditions than the non-catalytic, thermal reaction. The most active catalyst was the metallic Pt on Ti mesh, but the Pt leaching was significant. The specific activity of Ru/Ti was higher; moreover there was only negligible leaching even after 100 hours usage according to PGAA and ICP-MS measurements. The intermediates of the CWO of PAR were easily biodegradable. [1]

6. The conclusion based on surface investigation methods is that the Ru on the Ti mesh can be in the form of a Ru-oxide-titania composite or a titania supported Ru-oxide. The best specific activity of this catalyst in comparison with all monometallic and bimetallic versions on Ti mesh can be due to this species. [1-2]

Practical application possibilities

The combination of EB-WO can be tested at WWTPs where the EB method already has been applied in a routine manner (South-Korea, China), the design of a large scale reactor has to be solved in context with the electron accelerator.

Experiments of longer period are needed for the verification of the stability of the mesh catalysts and with real PWWs. The CWO reactions can be tested within pharmaceutical companies as there can be unused high pressure autoclaves designed for hydrogenation which can be adapted to WO reactions.

The experiences of DOE application in WO and CWO were utilized in the design of the scale-up experiments in the Swiss-Hungarian project.

PUBLICATIONS

Papers in journals underlying the dissertation

- [1] E. Szabados, Gy. Sági, F. Somodi, B. Maróti, D. F. Srankó, A. Tungler, Wet air oxidation of PAR over precious metal/Ti mesh monolith catalysts, J. Ind. Eng. Chem., DOI:10.1016/j.jiec.2016.11.005 (2015 IF: 4,179)
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- [3] E. Szabados, Gy. Sági, A. Kovács, E. Takács, L. Wojnárovits, A. Tungler, Comparison of catalysis and high energy irradiation for the intensification of WO as PWW pretreatment, React. Kinet. Mech. Cat. 116 (2015) 95-103 (2015 IF: 1,265, references: 1)

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- [4] A. Tungler, E. Szabados and A. M. Hosseini (2015). Wet Air Oxidation of Aqueous Wastes, Wastewater Treatment Engineering,

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Conference oral presentations and posters underlying the dissertation

1. „Testing of CWAO with design of experiments”, Antal Tungler, Erika Szabados, Emese Vágó, **Proceedings of „The 19th international symposium on analytical and environmental problems”**, 245-248, ISBN 978-963-315-141-9, 23 09 2013, Szeged (*poster presentation*)
2. „Modell szennyvíz nedves oxidációs reakcióinak vizsgálata kísérlettervek segítségével”, Szabados Erika, Tungler Antal, Pinke Balázs, Vágó Emese, **XXXVI. Kémiai Előadói Napok**, Katalízis I. Szekció, 29 10 2013, Szeged, ISBN: 978-963-9970-53-3 (*oral presentation in Hungarian*)
3. „Intensification the chemical treatment of pharmaceutical wastewater: CWAO and irradiation combined with wet air oxidation”, Erika Szabados, Antal Tungler, Sándor Kemény, **5th EUChemS Chemistry Congress**, 02 08 2014, Istanbul, Turkey (*oral presentation in English*)
4. „Hulladékvizek nedves oxidációjának intenzifikálása”, Szabados Erika, Tungler Antal, Kemény Sándor, Takács Erzsébet, Wojnárovits László, **XII. Oláh György Doktoráns Konferencia**, 05 02 2015, Budapest (*oral presentation in Hungarian*)
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(*oral presentation in Hungarian*)